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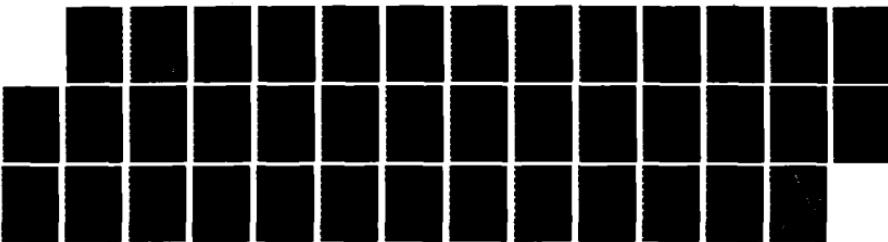
INVESTIGATIONS OF CHEMILUMINESCENCE AND OXIDATION
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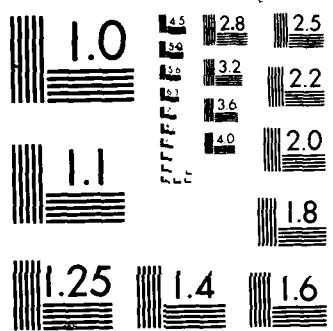
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Cosensitized electron-transfer photooxygenation has been developed in our laboratory as a new method for the photochemical oxidation of various organic substrates. Compounds which are relatively resistant to standard photo-oxygenation procedures can be oxidized by a process that utilizes a non-light-absorbing aromatic hydrocarbon (biphenyl, BP) as a catalyst or cosensitizer in conjunction with the cyano-substituted sensitizer, 9,10-dicyanoanthracene (DCA) and visible light (400-450 nm) in the presence of oxygen. Under this contract, we have investigated the photochemical conversion of epoxides, aziridines, and cyclopropanes to 1,2,4-trioxolanes (ozonides), 1,2,4-dioxazolidines, and 1,3-dioxolanes, respectively. Insight into the mechanism of the DCA- sensitized photooxygenation of epoxides and aziridines was obtained through a study of the stereochemistry of the reactions. The exclusive formation of the cis ozonide and cis 1,2,4-dioxazolidine from 2,3-diphenyloxirane and 2,3-diphenylaziridine has suggested a mechanism involving the addition of singlet oxygen as a dipolarophile to intermediate carbonyl and azomethine ylides. DCA-BP consensitized photooxygenation has also been utilized provide a new approach to the synthesis of chemiluminescent 1,2-dioxetantes.

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INVESTIGATIONS OF CHEMILUMINESCENCE
AND OXIDATION REACTIONS

FINAL REPORT

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15 July 1986

U. S. ARMY RESEARCH OFFICE
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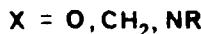
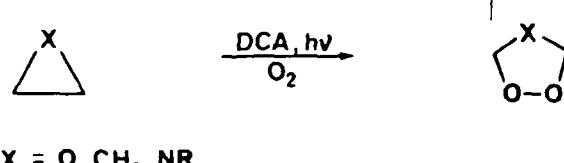
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ABSTRACT

Cosensitized electron-transfer photooxygenation has been developed in our laboratory as a new method for the photochemical oxidation of various organic substrates. Compounds which are relatively resistant to standard photooxygenation procedures can be oxidized by a process that utilizes a non-light-absorbing aromatic hydrocarbon (biphenyl, BP) as a catalyst or cosensitizer in conjunction with the cyano-substituted sensitizer, 9,10-dicyanoanthracene (DCA). Irradiation with visible light (400-450 nm) in the presence of oxygen promotes electron transfer from the cosensitizer to singlet excited DCA with subsequent generation of superoxide ion. Attack by this highly reactive species on the organic substrate or its radical cation effects the oxidation of the material.

Under this contract, we have investigated the photochemical conversion of epoxides, aziridines, and cyclopropanes to 1,2,4-trioxolanes (ozonides), 1,2,4-dioxazolidines, and 1,3-dioxolanes, respectively. Insight into the mechanism of the DCA-sensitized photooxygenation of epoxides and aziridines was obtained through a study of the stereochemistry of the reactions. The exclusive formation of the cis ozonide and cis 1,2,4-dioxazolidine from 2,3-diphenyloxirane and 2,3-diphenylaziridine has suggested a mechanism involving the addition of singlet oxygen as a dipolarophile to intermediate carbonyl and azomethine ylides. DCA-BP cosensitized photooxygenation has also been utilized to provide a new approach to the synthesis of chemiluminescent 1,2-dioxetanes.

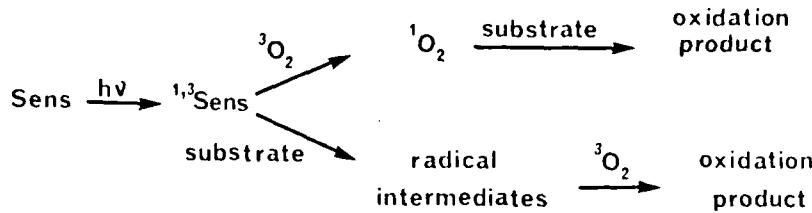


We have also developed a new polymer-immobilized chemical source of singlet oxygen. Photooxygenation of the polystyrene-bound naphthalene at -78°C results in an endoperoxide which cleanly liberates singlet oxygen on warming to ambient temperature.

SUMMARY OF ARO-SUPPORTED RESEARCH

1. Introduction - Mechanisms of Photooxygenation. Two general mechanisms for the oxidation of organic and biological substrates under the influence of light, oxygen, and a sensitizer have been identified (Scheme 1). One process involves the absorption of visible light by a sensitizer (usually a dye) with subsequent energy transfer to ground state oxygen to produce singlet oxygen ($^1\text{O}_2$). This metastable species exhibits high reactivity towards a variety of organic substrates including alkenes, dienes, aromatic hydrocarbons, and sulfides.¹ A second type of photosensitized oxygenation results from transfer of an electron or hydrogen atom in a direct interaction of the excited sensitizer and organic substrate. Reaction of the radical intermediates with oxygen yields the oxidation products.

Scheme 1



An example of this second type of oxidation process is electron-transfer photooxygenation with cyano-substituted aromatic sensitizers such as 9,10-dicyanoanthracene (DCA). DCA-sensitized oxygensations of alkenes, dienes, acetylenes, and sulfides have been reported.² Photooxygenations with DCA are carried out in polar solvents such as acetonitrile using 400 nm light. Quenching of singlet excited DCA by the substrate results in electron transfer and

formation of DCA^{\cdot} and the substrate radical cation. Although this electron-transfer process had been postulated from correlations of quenching rate constants and free energies of electron transfer^{3,4} and from solvent-dependent exciplex emissions,⁵ the first direct evidence for the photochemical generation of the DCA radical ion was provided by our group.^{6,7} The ESR spectrum of this species was observed upon irradiation of solutions of DCA and various quenchers in deoxygenated acetonitrile (Figure 1). The spectrum was identical to that reported by Brunner and Dörr for DCA^{\cdot} prepared by metal/ammonia reduction.⁸

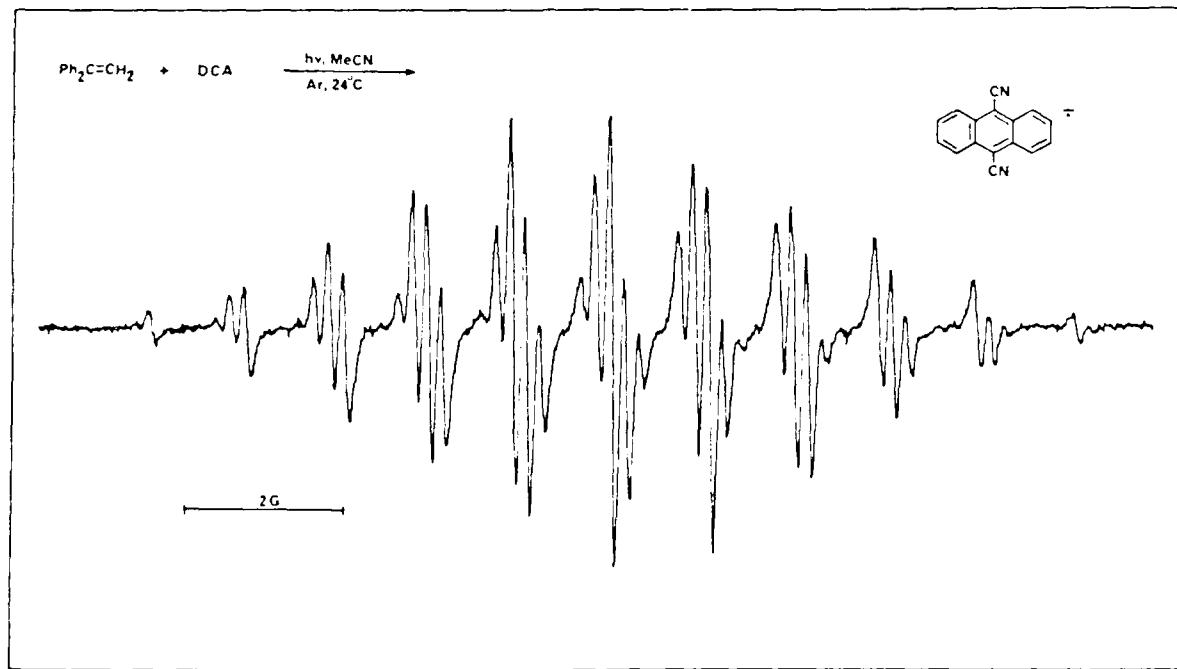


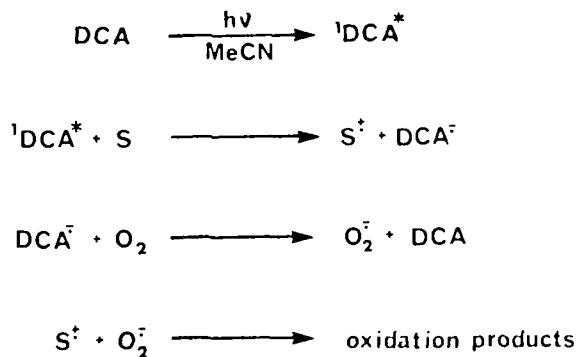
Figure 1. ESR spectrum of DCA^{\cdot} obtained by photolysis of a solution of DCA (5×10^{-4} M) and 1,1-diphenylethylene (10^{-2} M) in dry acetonitrile under Ar.

The free energy change (ΔG) involved in the electron-transfer quenching of $^1\text{DCA}^*$ is given by the Weller³ equation:

$$\Delta G = 23.06 [E(S/S^\cdot) - E(DCA^\cdot/DCA) - e_o^2/a\epsilon - \Delta E_{o,o}]$$

where $E(S/S^\cdot)$ is the oxidation potential of substrate, $E(DCA^\cdot/DCA)$ is the reduction potential of the sensitizer, $e_o^2/a\epsilon$ is the energy gained by bringing the two radical ions to encounter distance a in the solvent of dielectric constant ϵ (~ 0.06 eV in MeCN), and $\Delta E_{o,o}$ is the electronic excitation energy of DCA. For DCA where $E(DCA^\cdot/DCA) = -0.98$ V vs. SCE in MeCN and $\Delta E_{o,o} = 2.89$ eV, Foote has calculated that electron-transfer quenching of $^1\text{DCA}^*$ should be exothermic for substrates with oxidation potentials less than 2 V relative to SCE.⁴ Subsequent steps in the mechanism for electron-transfer photooxygenation are: (1) transfer of an electron from DCA^\cdot to oxygen to generate O_2^\cdot and (2) reaction of O_2^\cdot with S^\cdot to yield the peroxidic products.

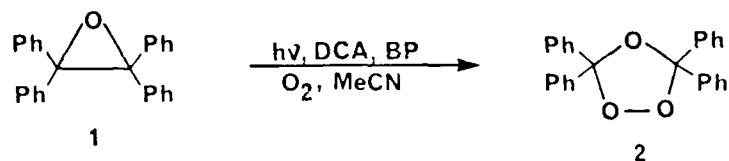
Scheme 2



Until recently, photooxygenations by the above process were limited to those substrates that quench the fluorescence of DCA. However, a method has now been developed by our group for the electron-transfer photooxygenation of compounds that have oxidation potentials greater than 2 V and that consequently do not quench singlet excited DCA.⁹ For example, epoxides that are unreactive under standard DCA-sensitized conditions can be readily converted to the corresponding

ozonides in high yield by use of a non-light-absorbing aromatic hydrocarbon (biphenyl, BP) as a catalyst or cosensitizer in conjunction with DCA.⁹⁻¹³ It should be noted that BP is not consumed in these reactions. Recent studies have shown that DCA-BP cosensitization can provide dramatically enhanced rates of photooxygenation for a wide variety of substrates.

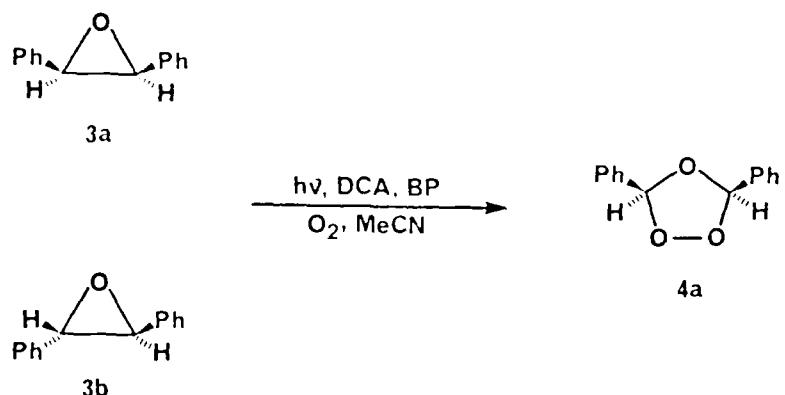
2. Photochemical Conversion of Epoxides to Ozonides. Our ARO-supported research on photooxygenation resulted in the first report of the photochemical conversion of an epoxide to an ozonide.⁹ The photooxygenation of tetraphenyl-oxirane (1) was initially carried out in acetonitrile with only DCA as the sensitizer. Although the reaction required over 40 h irradiation with a 450-W Hg lamp, ozonide 2 could be isolated in 51% yield. The slow rate of the reaction



was not surprising as 1 exhibits an oxidation potential above 2 V and does not measurably quench the fluorescence of DCA in acetonitrile. We found, however, that a significant enhancement in the rate of the DCA-sensitized photooxygenation of epoxide 1 was observed in the presence of biphenyl (BP). Addition of 1×10^{-2} M BP to the reaction solution resulted in complete conversion of 1 in 10 min and formation of 93% ozonide 2. Control experiments have shown that: (1) no oxidation occurs in the absence of DCA; (2) BP is not consumed in the reaction; (3) ozonide 2 is stable to the photooxygenation conditions and (4) epoxide 1 is not oxidized upon irradiation with a 400-W high-pressure sodium lamp with Rose Bengal in acetonitrile, indicating that 1 does not react with $^1\text{O}_2$ directly.

Insight into the mechanism of this reaction was obtained by an investigation of the DCA-BP cosensitized photooxygenation of cis-2,3-diphenyloxirane (3a) and

and trans-2,3-diphenyloxirane (3b).¹¹ We observed that photooxygenation of 3a and 3b gives rise exclusively to the *cis* ozonide 4a. Authentic samples of *cis*- and trans-3,5-diphenyl-1,2,4-trioxolane (4a and 4b, respectively) were obtained from a mixture prepared by ozonation of trans-stilbene.



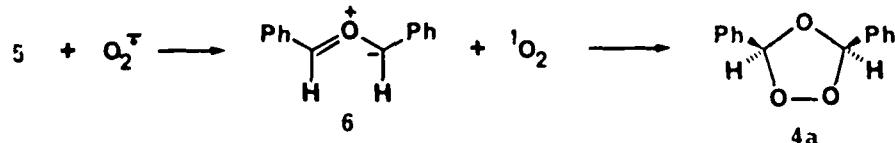
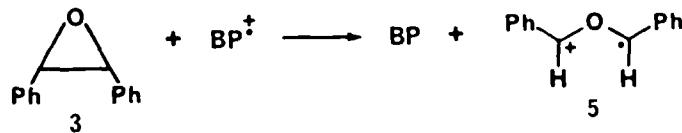
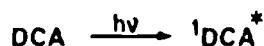
We have proposed that BP acts as a cosensitizer in photooxygenations by a process analogous to homogeneous redox catalysis for electrode reactions.¹⁰

Epoxides 1 and 3 do not quench the fluorescence of DCA in MeCN as is expected for compounds with oxidation potentials greater than 2 V vs. SCE (trans-2,3-diphenyloxirane (3b), $E_p^{\text{OX}} = 1.89$ V vs. Ag/AgNO₃ in MeCN¹⁴; ~ 2.2 V vs. SCE in MeCN). However, BP is more easily oxidized ($E_p^{\text{OX}} = 1.90$ V vs. SCE in MeCN) than the epoxides and therefore quenches ${}^1\text{DCA}^\bullet$ more efficiently (k_q for BP = $3.1 \times 10^9 \text{ M}^{-1} \text{s}^{-1}$) to generate DCA⁺ and BP⁺. Although energetically unfavorable, a reversible electron transfer from the epoxides to BP⁺ could generate the unopened epoxide radical cation. This step would be driven by the subsequent formation of the ring-opened radical cation and irreversible reaction with O₂^{·-} to yield the ozonide (Scheme 3).

Of additional interest are the mechanistic implications of the exclusive formation of *cis* ozonide 4a from both epoxides 3a and 3b. These results are not consistent with a mechanism involving attack of O₂^{·-} on epoxide radical cation 5 to give long-lived biradical or zwitterion intermediates. Such

mechanisms would predict the formation of a mixture of isomeric ozonides. A plausible mechanism that is consistent with the stereoselective formation of ozonide 4a involves: (1) formation of the most stable E,E-conformation of epoxide radical cation 5 from either 3a or 3b; (2) subsequent reduction of 5 by O_2^- (or DCA $^-$) to yield the E,E-isomer of carbonyl ylide 6; and (3) $4 + 2$ cycloaddition with 1O_2 acting as a dipolarophile. Foote has shown that 1O_2 can be formed in DCA-sensitized photooxidation hv energy

Scheme 3



transfer from singlet and triplet excited DCA to oxygen.¹⁵ Singlet oxygen could also be generated as a result of the electron transfer from O_2^- to 5.¹⁶

Experiments are in progress to evaluate the role of 1O_2 and ylides in this reaction. However, the proposed intermediacy of carbonyl ylide 6 is in accord with observations of several groups on the trapping of photogenerated carbonyl ylides.^{14,17} For example, Griffin^{17a} has recently shown that direct photolysis or thermolysis of 2,3-diaryloxiranes such as 3a and 3b generates carbonyl ylides

that can be trapped by dipolarophiles to afford substituted tetrahydrofurans.

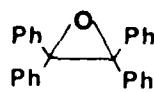
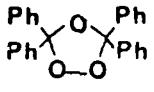
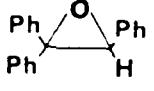
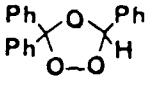
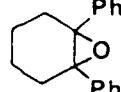
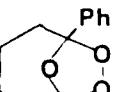
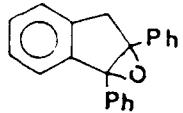
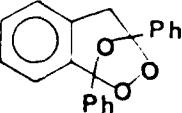
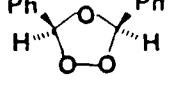
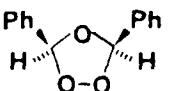
As in the present study, the major products arise from a 4 + 2 cycloaddition of the dipolarophiles to the thermodynamically more stable E,E-carbonyl ylides. In related work, Arnold¹⁴ has utilized 1,4-dicyanonaphthalene as an electron-transfer sensitizer with epoxides 3 in the presence of dipolarophiles to yield substituted tetrahydrofurans in which the major products have a cis-diphenyl relationship. The proposed mechanism involves formation of the epoxide radical cation followed by back electron transfer from the sensitizer radical anion to give the carbonyl ylide.¹⁸ Trozzolo and Griffin have used spectroscopic methods to characterize carbonyl ylides produced by the photochemical cleavage of epoxides.¹⁹

Additional examples of the photochemical conversion of epoxides to ozonides are shown in Table 1. It should be noted that the ozonide derived from 1,2-diphenylcyclohexene oxide was previously unknown as ozonation of the corresponding alkene does not yield the ozonide. These results indicate that interesting new ozonides may now be accessible through DCA-BP cosensitized photooxygenation of epoxides.

Related studies have shown that certain epoxides which exhibit low oxidation potentials because of electron-donating groups or ring strain can be oxidized by DCA directly.^{20,21} Of concern, however, was the report by Ohta that trans ozonides are formed from the photooxygenation of 2,3-bis(4'-methoxyphenyl)oxirane and other epoxides.²⁰ The results described below suggest that the stereochemical assignments by Ohta are probably incorrect.

In order to evaluate any possible influence of the cosensitizer on the stereochemistry of these reactions, we conducted a study of the stereochemistry of the DCA-sensitized photooxygenation of dinaphthyl epoxides which undergo oxygenation in the absence of BP (E_p^{OX} for 7 and 8 = 1.50 - 1.59 V vs. SCE in MeCN; k_q for DCA = $1.37 - 1.54 \times 10^{10} M^{-1} s^{-1}$). We find that cis and trans epoxides 7 and 8 also yield exclusively cis ozonides. The photo-ozonides 9 were isolated

Table 1. Cosensitized Electron-Transfer Photooxygenation of Epoxides

Epoxide ^a	Ozonide	Yield (%)	Mp (°C)
		93%	168-9
		90%	95-6
		88%	105-6
		85%	124-5
		65%	98-100
		65%	98-100

^aThe epoxides are inert to prolonged photooxygenation with DCA in the absence of biphenyl with the exception of 2,3-diphenylindene oxide which produced the corresponding ozonide in 4 h in 70% yield. This epoxide quenches DCA fluorescence as efficiently as biphenyl ($k_q = 3.2 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$).

by preparative TLC on silica and recrystallized (Table 2). Control experiments have shown that the ozonides are stable to the photooxygenation conditions and no isomerization of the epoxides occurs during the reaction. For comparison, a sample of trans-2,3-bis(2'-naphthyl)-1,2,4-trioxolane (10b) was prepared by ozonation of 1,2-bis(2'-naphthyl)ethene.

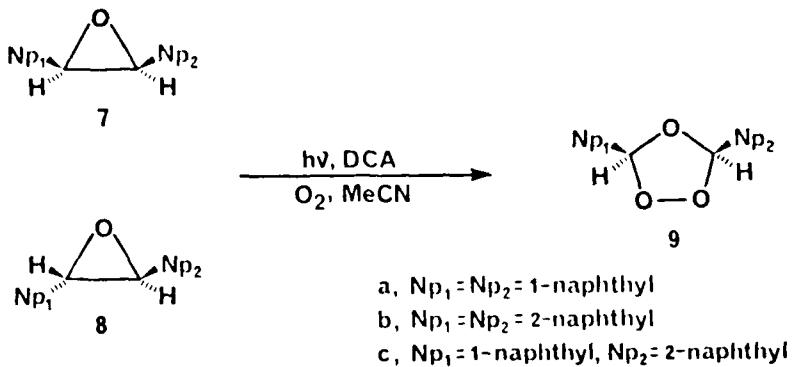


Table 2. Properties of Naphthyl-Substituted Ozonides

Ozonide	Isolated yield from photoox. (%) (NMR yield) ^a	mp (°C)
<u>cis</u> <u>9a</u>	78 (89)	87-9
<u>cis</u> <u>9b</u>	75 (89)	172-4
<u>trans</u> <u>10b</u>	—	166-8
<u>cis</u> <u>9c</u>	35 ^b (80)	108-10

^aNMR yields were determined using an internal standard. ^bThis ozonide appears to be rather unstable and suffers decomposition during isolation.

In our earlier study of the cosensitized photooxygenation of cis- and trans-2,3-diphenyloxirane, we had compared the resulting photo-ozonide to authentic cis and trans ozonide prepared by ozonation of stilbene. The stereochemistry of these ozonides had been assigned by Criegee by chromatography over cellulose

acetate.²² The chiral trans ozonide was identified by its partial resolution on this stationary phase. Murray and coworkers had earlier used kinetic resolution by brucine to identify the trans isomer of diisopropyl ozonide.²³

In order to establish the stereochemistry of the naphthyl-substituted ozonides, we have conducted similar experiments utilizing high-performance liquid chromatography over optically active (+)-poly(triphenylmethyl methacrylate).²⁴ As anticipated, 10b obtained from ozonation of 2,3-bis(2'-naphthyl)ethene was resolved by chromatography over this stationary phase (Figure 2A), confirming the trans dinaphthyl stereochemistry of this ozonide. Chromatography of the photo-ozonides 9a and 9b exhibited only one peak consistent with the proposed cis stereochemistry. Any remaining uncertainty regarding the structure of the photo-ozonides has been removed by X-ray crystallography of a single crystal of ozonide 9b (Figure 2B). These results demonstrate that the same stereochemical

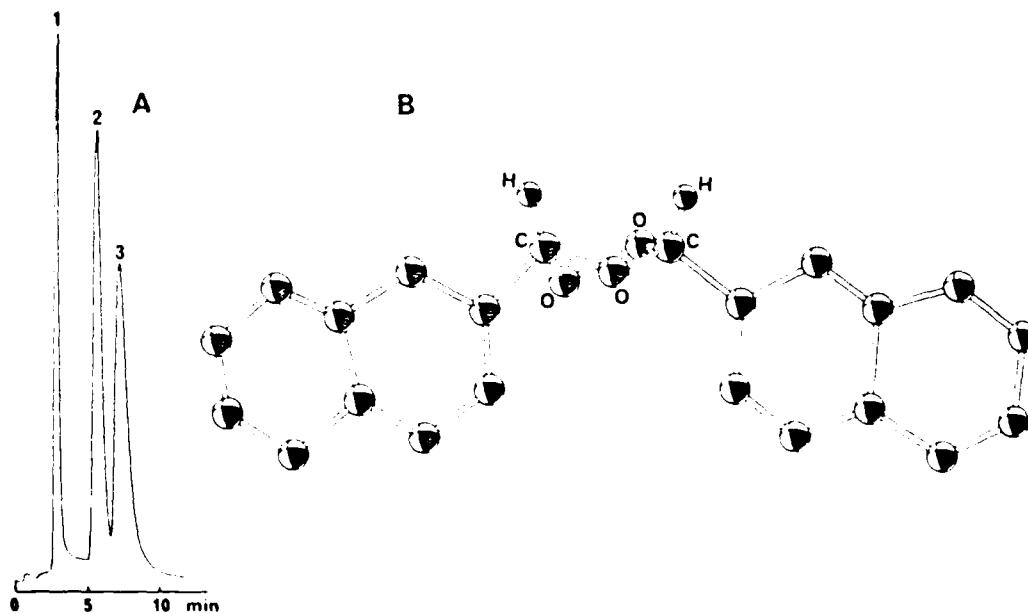
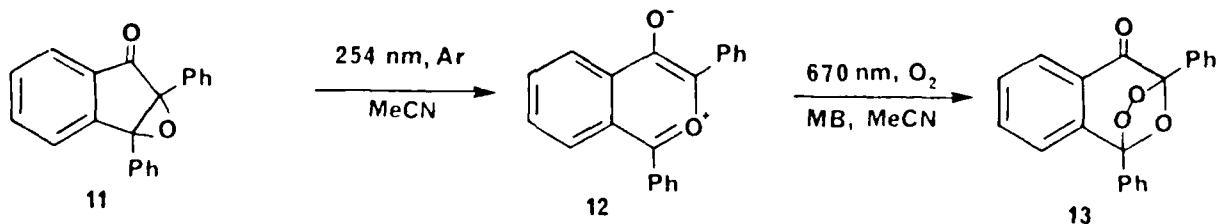


Figure 2. A. Chromatographic resolution of trans-3,5-bis(2'-naphthyl)-1,2,4-trioxolane (10b) on a μ S-Chiralpak OJ(+) column using MeOH as eluent. Peak 1 results from a trace impurity of 2-naphthaldehyde; the extinction coefficient at 254 nm is much larger for the aldehyde than the ozonides. Peaks 2 and 3 show the separated enantiomers of the trans ozonide.

B. X-ray structure of cis-3,5-bis(2'-naphthyl)-1,2,4-trioxolane (9b).

course is followed for electron-transfer photooxygenation of easily oxidized 1,2-diaryl-substituted epoxides as for DCA/BP cosensitized photooxygenation.

3. Formation of an Ozonide by Addition of Singlet Oxygen to a Stabilized Carbonyl Ylide. The striking stereochemical results of the electron-transfer photooxygenation of 1,2-diaryloxiranes have led us to propose a mechanism for this reaction involving the addition of singlet oxygen as a dipolarophile to an intermediate carbonyl ylide. We have, therefore, recently investigated the addition of singlet oxygen to the stabilized ylide 12 formed by photolysis of 2,3-diphenylindenone oxide (11). Several years ago Ullman demonstrated that epoxide 11 and ylide 12 are photochemically interconvertible.²⁵ Irradiation of 11 with ultraviolet light results in a deep red solution of pyrylium oxide 12. Subsequent exposure to visible light regenerates 11. Ullman also found that photolysis of 11 in the presence of oxygen yielded products that could be explained in terms of the decomposition of an intermediate ozonide. We have reexamined this reaction and obtained the first direct evidence for the formation of an ozonide from a dipolar cycloaddition of singlet oxygen to a carbonyl ylide. Ground state oxygen also reacts with 12 to give 13 but at a much slower rate.

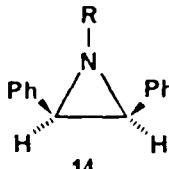
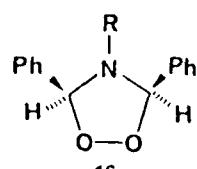
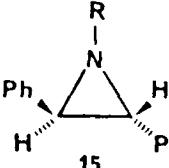
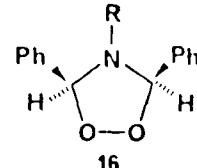


Solutions of epoxide 11 in MeCN were deoxygenated with argon. Irradiation in a quartz cuvette with a low pressure Hg lamp afforded intense red solutions of ylide 12 (λ_{max} in MeCN = 535 nm). After generation of the ylide, a solution

of methylene blue (MB) in MeCN was added (λ_{max} of MB = 655 nm). The resulting solution was simultaneously bubbled with oxygen and irradiated at 670 nm using a 150-W Varian EIMAC Illuminator and monochromator. Reverse phase HPLC indicated the formation of ozonide 13 in greater than 95% yield (based on reacted 11). MB was chosen as the singlet oxygen sensitizer for these experiments because it could be selectively excited at 670 nm in the presence of the ylide. A control experiment in which oxygen was bubbled through a solution of 12 in the dark was carried out. HPLC analysis showed that only 3% of 13 had been formed (based on reacted 11). Additional studies of this system are in progress. However, these preliminary results demonstrate that $^1\text{O}_2$ is highly reactive towards carbonyl ylides.

4. Photochemical Conversion of Aziridines to 1,2,4-Dioxazolidines. Our results on the photooxygenation of epoxides have led us to investigate the DCA-sensitized reaction of other heterocycles. The studies resulted in the first report of the electron-transfer photooxygenation of aziridines and the isolation of the resulting 1,2,4-dioxazolidines.^{26,27} Unlike the corresponding diphenyl-substituted epoxides which do not quench the fluorescence of DCA and consequently are unreactive in the absence of biphenyl, the more easily oxidized aziridines efficiently quench $^1\text{DCA}^*$ and react without the addition of the cosensitizer ($E_p^{\text{OX}} = 1.5-1.7$ V, $k_q = 8.2-11 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$). The stereochemistry of the photooxygenation of cis-2,3-diphenylaziridine (14a) and trans-2,3-diphenylaziridine (15a) does, however, parallel that observed with the corresponding epoxides (Table 3). We have found that only the cis 1,2,4-dioxazolidine 16a is formed from the DCA-sensitized oxygenation of 14a and 15a. In contrast, photooxygenation of N-alkyl-substituted 2,3-diphenylaziridines provides both isomers of the peroxide. The cis/trans ratio of isomers decreases with increasing size of the group on nitrogen.

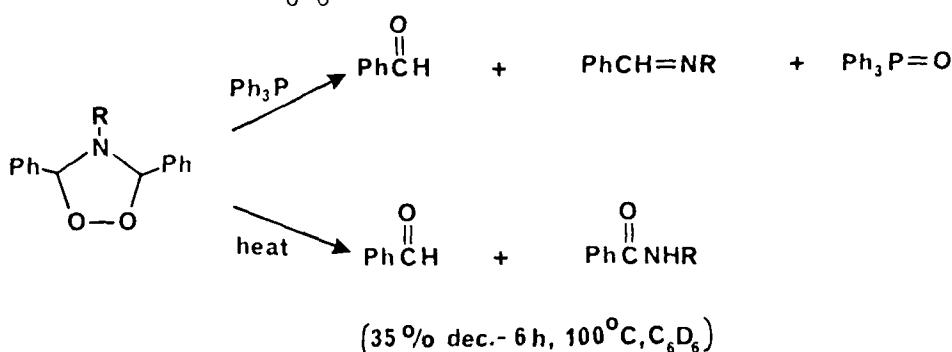
Table 3. Electron-Transfer Photooxygenation of Aziridines.

Aziridine	$E_p^{\text{OX}} \text{ (V)}^a$	$k_q \text{ (M}^{-1} \text{ s}^{-1}\text{)}^b$	1,2,4-Dioxazolidines (Ratio of Isomers) ^c		
 14			 16		
<u>14a</u> , R = H	1.64	7.8×10^9	100	:	< 1
<u>14b</u> , R = Et	1.66	7.4×10^9	87	:	13
<u>14c</u> , R = Me	1.55	8.7×10^9	85	:	15
<u>14d</u> , R = n-Bu	1.70	8.2×10^9	87	:	13
<u>14e</u> , R = PhCH ₂	1.65	8.6×10^9	40	:	60
<u>14f</u> , R = t-Bu	1.73	8.5×10^9	< 1	:	100
 15			 16		
<u>15a</u> , R = H	1.50	1.1×10^{10}	100	:	< 1
<u>15b</u> , R = Et	1.73	-	86	:	14

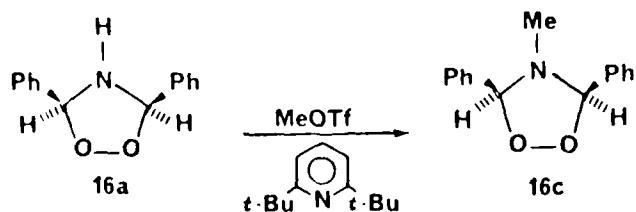
^aPeak potentials vs. SCE for the irreversible oxidation of the aziridines. ^bRate constants for quenching of DCA fluorescence in nitrogen-saturated MeCN. ^cProducts were determined by 300 MHz ¹H NMR using an internal standard.

Photooxygenations of the aziridines shown in Table 3 were carried out in oxygenated MeCN with 1×10^{-2} M substrate and 6×10^{-4} M DCA. Reactions were complete in 1.5-3 h as determined by reverse phase HPLC. The products were analyzed by removal of the solvent at 0°C under vacuum and acquiring NMR spectra

in CDCl_3 . We have found that the ratio of isomers is independent of reaction time and that 16 and 17 are not significantly decomposed under the reaction conditions. No isomerization of the starting aziridines was detected during photolysis. The dioxazolidines have been characterized by reduction with $\text{Ph}_3\text{P}^{\ddagger}$ to yield benzaldehyde and the corresponding imines. These peroxides are remarkably stable to thermolysis exhibiting slow decomposition to benzaldehyde and amides upon heating in C_6D_6 .



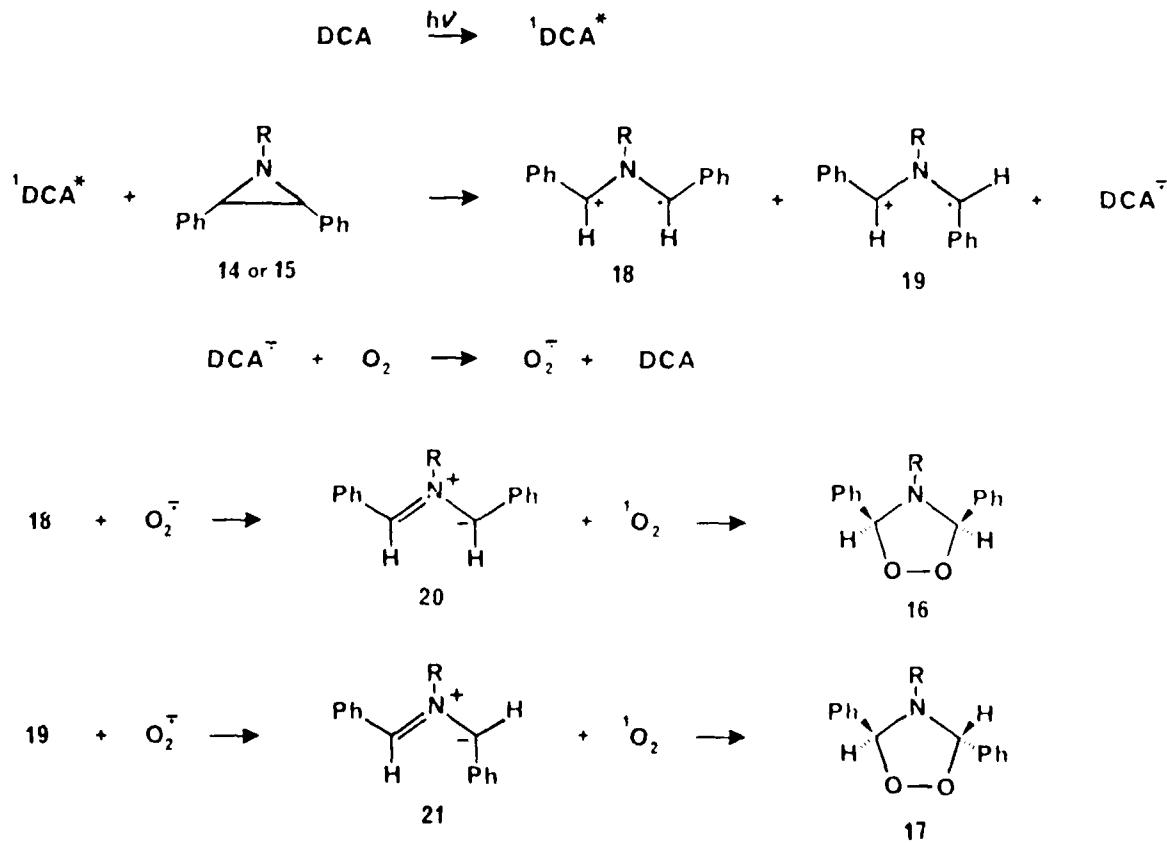
The stereochemistry of the dioxazolidines has been unambiguously established by the following observations. Photooxygenation of cis-1-benzyl-2,3-diphenyl-aziridine (14e) in MeCN gave two peroxides with an isomeric ratio of 40:60. The minor cis isomer 16e exhibited two 2H singlets at δ 5.673 and 4.102 while the major trans isomer 17e exhibited a 2H singlet at δ 5.886 and a 2H AB quartet for the diastereotopic N-benzyl protons at δ 3.700 and 3.779 ($J = 13.2$ Hz). These results indicated that ring protons for the cis dioxazolidines appear at higher field and were used to stereochemically assign the other dioxazolidines. As only one isomer was observed from the photooxygenation of the N-unsubstituted aziridines 14a and 15a, the chemical shift of the ring protons could not be used to assign the structure of this peroxide. However, treatment of the N-unsubstituted



dioxazolidine in CDCl_3 with 1.2 equivalents of methyl triflate in the presence of 2,6-di-*t*-butylpyridine afforded in 80% yield the *cis* isomer 16c of the N-methyldioxazolidine.

We have suggested that the stereoselective formation of *cis* ozonides from *cis* and *trans*-2,3-diaryloxiranes could be rationalized in terms of a mechanism involving concerted addition of $^1\text{O}_2$ to an intermediate carbonyl ylide. A similar mechanism is proposed for the DCA-sensitized photooxygenation of aziridines with addition of $^1\text{O}_2$ as a dipolarophile to azomethine ylides (Scheme 4). Support for this mechanism is provided by the stereochemical results presented in Table 3. The *cis* dioxazolidine 16a is formed exclusively from 14a and 15a by trapping the more stable ylide 20 ($\text{R} = \text{H}$). However, the presence of substituents on nitrogen sterically destabilizes ylide 20 and its radical ion precursor 18 leading to an isomeric mixture of dioxazolidines that is a function of the size of the group on nitrogen.

Scheme 4



The proposed intermediacy of carbonyl and azomethine ylides in the electron-transfer photooxygenation of epoxides and aziridines is as yet only a working hypothesis which adequately explains the observed results. This mechanism is, however, in agreement with the extensive literature on the trapping of photolytically and thermally generated ylides by dipolarophiles.¹⁷

5. Photochemical Conversion of Cyclopropanes to 1,2-Dioxolanes. We have also examined the DCA-sensitized photooxygenation of aryl-substituted cyclopropanes and have observed the formation of 1,2-dioxolanes (Table 4). The products from these reactions were isolated by chromatography and characterized spectroscopically. The stereochemical results from the photooxygenation of cis- and trans-1,2-dimethyl-1,2-diphenylcyclopropane suggest that the formation of the dioxolanes occurs stepwise, perhaps via biradical intermediates. The photooxygenation of a mixture of the isomeric 1,2-diphenylcyclopropanes led to the formation of a ketoalcohol. This result is in agreement with the observations of Mizuno.²⁸ It is possible that this product arises by decomposition of an intermediate 1,2-dioxolane.

Although these cyclopropanes are more easily oxidized than biphenyl (BP) and consequently quench the fluorescence of DCA at faster rates (Table 4). Nevertheless, addition of BP as a cosensitizer to these reactions decreases the reaction times by an order of magnitude. The mechanism for the rate enhancement observed with BP is discussed in Section IV-1, page 33.

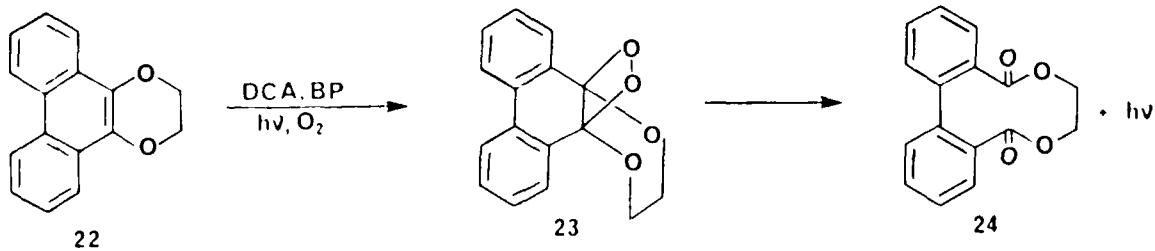
Table 4. Cossensitized Electron-Transfer Photooxygenation of Cyclopropanes

Cyclopropane	E_p^{ox} (V) ^a	k_q ($M^{-1} s^{-1}$) ^b	Products (yields, %) ^c
	1.48	1.1×10^{10}	 (35%) (59%)
	1.70	7.9×10^9	 (70%)
	1.90	9.4×10^9	 (28%) (46%)
	1.85	9.7×10^9	 (27%) (47%)
	-	-	 (80%)

^aPeak potentials for the irreversible oxidation of the cyclopropanes were obtained by cyclic voltammetry in MeCN vs. SCE: Pt electrode, 0.1 M tetraethylammonium perchlorate, scan rate = 900 mV s⁻¹. ^bRate constants for the quenching of DCA fluorescence in nitrogen-saturated MeCN. ^cYields were determined by ¹H NMR using phthalide as an internal standard.

6. Synthesis of a Chemiluminescent 1,2-Dioxetane by Cossensitized Electron-Transfer Photooxygenation. We have found that DCA-BP cossensitized photooxygenation can be used to produce a highly chemiluminescent 1,2-dioxetane. 1,4-Phenanthro-dioxene (22) was recently synthesized in our laboratory. Of interest was the preparation of dioxetane 23 by photooxygenation. However, we found that 22 was unreactive both towards singlet oxygen and electron-transfer photooxygenation with DCA. This latter observation was rather surprising as 22 exhibits a low oxidation potential (reversible one-electron oxidation at 1.01 V vs. SCE in MeCN) and quenches the fluorescence of DCA at a diffusion-controlled rate ($k_q = 2.4 \times 10^{10} M^{-1} s^{-1}$). However, in the presence of BP ($1 \times 10^{-2} M$) and DCA ($6 \times 10^{-4} M$) the photooxygenation of 22 proceeds rapidly to yield 1,2-dioxetane 23. The cossensitization by BP in this reaction is similar to the rate enhancement found in the photooxygenation of the aryl cyclopropanes. In both cases the substrates are more easily oxidized than BP and quench the fluorescence of DCA more efficiently (see Section IV-1, page 33).

The decomposition of this peroxide in MeCN at elevated temperatures to form bis lactone 24 ($t_{1/2}$ at $77^\circ C = 6$ min) is accompanied by intense chemiluminescence. We have previously observed that heterogeneous materials such as silica gel can be used to catalyze the cleavage of aryl-substituted dioxetanes.²⁹ This process was found to significantly increase the chemiluminescence efficiencies. The catalyzed decomposition of 23 is currently under study.



7. Polymer-Immobilized Endoperoxides - A Recyclable Source of Singlet Oxygen.

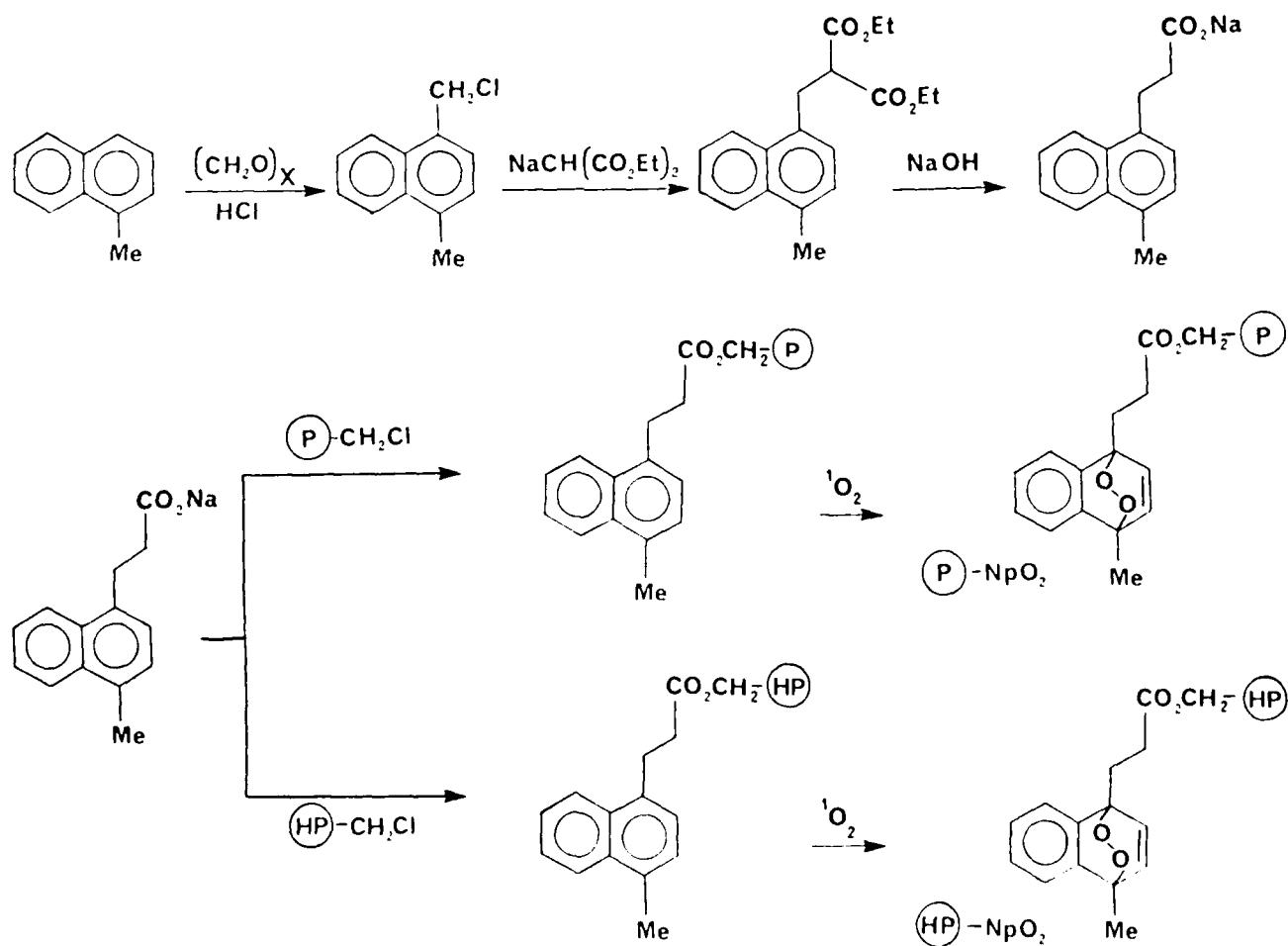
Singlet oxygen ($^1\text{O}_2$) reacts with a wide variety of organic and biological substrates.¹ Although this species can be generated by irradiation of a dye with visible light in the presence of oxygen, there are various applications for which an efficient chemical source of $^1\text{O}_2$ would be useful. Ideally, such a source would: (1) generate $^1\text{O}_2$ under mild conditions (ambient temperature) in a variety of solvents; (2) provide $^1\text{O}_2$ "cleanly" without formation of other reactive species such as superoxide and hydroxyl radical; (3) allow for convenient workup of oxygenation reactions and isolation of products; and (4) be recyclable. Our experience with polymer-immobilized photosensitizers³⁰ has led us to develop a useful chemical source of $^1\text{O}_2$ that meets the above criteria.³¹

Extensive literature exists on the reversible addition of $^1\text{O}_2$ to polynuclear aromatic hydrocarbons.³² Photooxygenation (either direct irradiation or dye sensitized) of these substrates affords endoperoxides which can subsequently be decomposed thermally to regenerate $^1\text{O}_2$. Although anthracene endoperoxides have been found to efficiently produce $^1\text{O}_2$, temperatures of 80-100°C are required. Naphthalene derivatives, on the other hand, liberate $^1\text{O}_2$ at more moderate temperatures. One remaining problem, however, with this chemical source of $^1\text{O}_2$ would be the difficulty in separating the resulting naphthalene from the desired oxygenation product. To solve this problem, we have developed two polymer-immobilized naphthalene derivatives that can be photochemically converted to the corresponding endoperoxides. These materials can be stored at -20°C with no loss of oxygen but used to produce $^1\text{O}_2$ in organic or aqueous solutions at ambient temperature. Only a simple filtration of the reaction solution is required to separate the product from the polymer beads. This polymeric material can be photochemically recycled and used again for oxygenation reactions.

The preparation of the polymeric singlet oxygen generators is described in Scheme 5. The carboxylate derivative of 4-methylnaphthylpropanoic acid was

attached by nucleophilic displacement to two chloromethylated polymers: a styrene-based polymer^{30b} ($\text{P}-\text{CH}_2\text{Cl}$) and a copolymer^{30a} ($\text{HP}-\text{CH}_2\text{Cl}$) of the mono-ethylene glycol ester of methacrylic acid and p-chloromethylstyrene. These polymer beads are crosslinked and are, therefore, insoluble in photo-oxygenation solvents. The polystyrene-based naphthalene ($\text{P}-\text{NP}$) is hydrophobic and compatible with organic solvents such as methylene chloride and toluene. For $^1\text{O}_2$ -mediated oxygenations in water or alcohols, the endoperoxide of the hydrophilic $\text{HP}-\text{Np}$ material is the reagent of choice.

Scheme 5



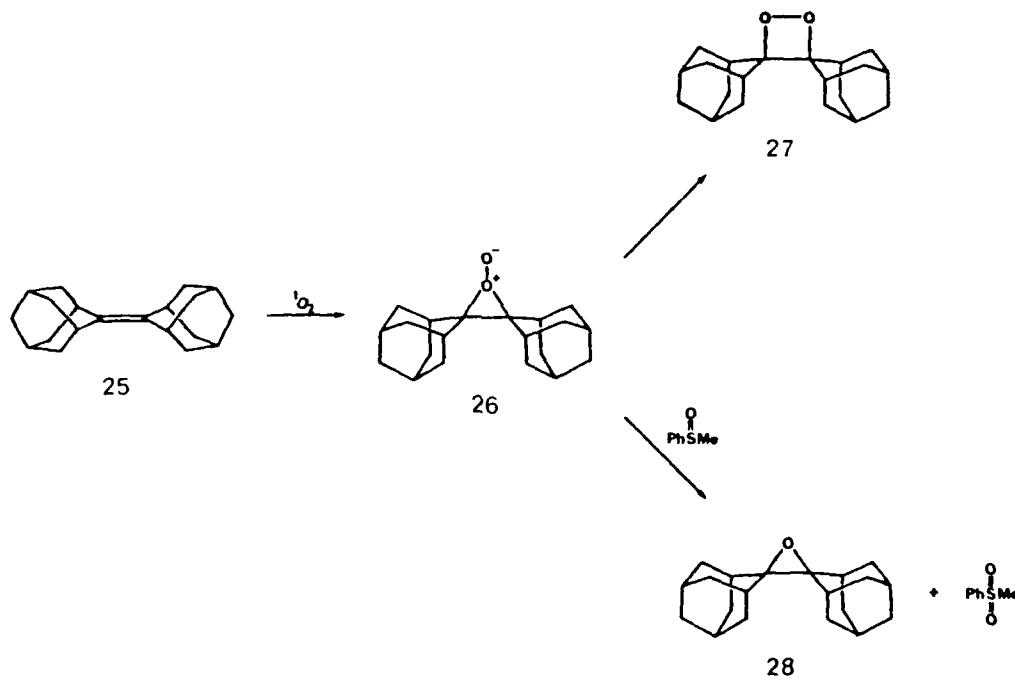
The polymers are oxygenated by irradiating a suspension of the beads at 0°C in acetone using Rose Bengal as the sensitizer. A 400-W high pressure sodium lamp is used as the light source. When the oxygen uptake is complete, the irradiation is discontinued and the polymer beads are filtered from solution. These oxygenated beads can be stored indefinitely at -20°C. A typical oxygenation of a substrate is carried out by adding 2-3 equivalents of the appropriate polymer-immobilized endoperoxide to a solution of the substrate at 25-35°C ($\tau_{1/2} = 45$ min at 30°C). After complete evolution of 1O_2 from the endoperoxide, the polymer beads are separated from the reaction by filtration. The oxygenation products are subsequently isolated by standard methods. Typical examples of oxygenations carried out with these new materials are shown in Table 5. Preliminary experiments have shown that > 50% of the oxygen released by the polymeric endoperoxides can be trapped as 1O_2 . Samples of the polymer beads have been recycled five times.

Table 5. Oxygenation of Substrates with Polymer-Immobilized Naphthalene Endoperoxides

Substrate	Product ^a	Polymeric Endoperoxide	Solvent
$\text{Me}_2\text{C}=\text{CMe}_2$		(P)-NpO ₂	PhMe
		(P)-NpO ₂	PhMe
		(P)-NpO ₂	PhMe
		(HP)-NpO ₂	DMSO
		(HP)-NpO ₂	H ₂ O
		(HP)-NpO ₂	MeOH

^aYields of the oxygenation products based on starting material were > 90%.

8. Evidence for a Perepoxide Intermediate in the 1,2-Cycloaddition of Singlet Oxygen to Adamantylideneadamantane. Singlet oxygen ($^1\text{O}_2$) reacts with adamantylideneadamantane (25) to afford the unusually stable 1,2-dioxetane 27.³³ Under certain conditions the photooxidation of 25 can yield the corresponding epoxide in addition to the dioxetane.³⁴ The mechanism for the formation of 27, and in particular 28, has been a subject of considerable controversy.³⁵ However, we were recently able to demonstrate that the key intermediate in this reaction is perepoxide 26. This species can be quantitatively trapped by nucleophilic oxygen-atom transfer to sulfoxides to yield sulfones and 28.³⁶



The nucleophilic character of perepoxide 26 is illustrated by the results of an investigation of substituent effects on the trapping reaction. A series of competition experiments with substituted-phenyl methyl sulfoxides gave relative reactivities for the co-oxidation of these sulfoxides during the photooxygenation of 25 in benzene: m-Cl, 1.4; p-Cl, 1.3; H, 1; p-Me, 0.79; p-OMe, 0.68. A Hammett plot of the logarithm of these rates against σ gave a ρ -value of +0.52, $r = 0.995$ (Figure 3). These results are consistent with theoretical studies of

Dewar³⁷ and Kearns³⁸ which predicted that a perepoxide would be a very polar species with significant negative charge on the exocyclic oxygen atom. A comparison of 26 to other nucleophilic oxygen-transfer intermediates is shown in Table 6. Our observations on the reaction of perepoxide 26 with sulfoxides parallel those of Foote³⁹ who reported the trapping of a persulfoxide ($\text{Et}_2^+\text{S}(\text{O})\text{O}^-$) by sulfoxides.

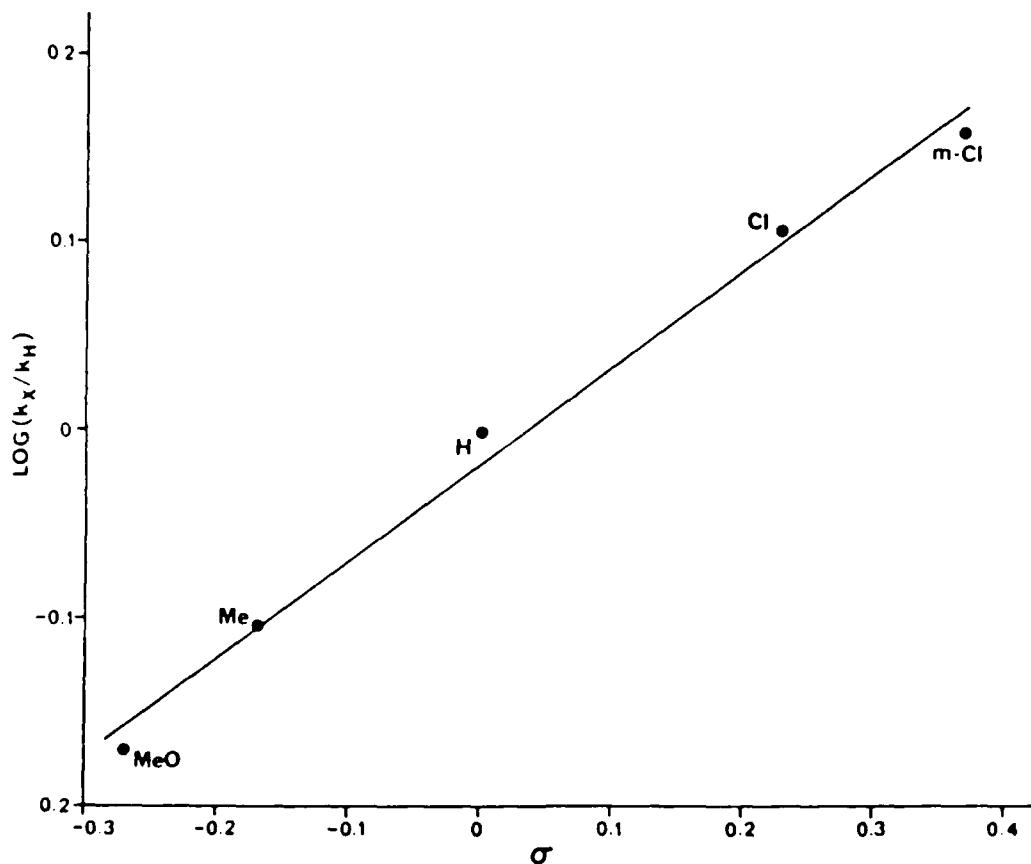
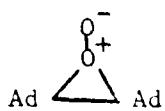
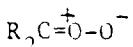
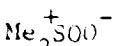
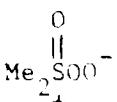


Figure 3. Hammett plot of the logarithm of the relative rates for the photosensitized co-oxidation of $\text{X-C}_6\text{H}_4\text{SOMe}$ in the presence of adamantlylideneadamantane (26) against substituent constants σ . Substituents are para except where noted.

Table 6. Nucleophilic Oxygen-Atom Transfer to Sulfoxides

oxygen-atom donor	sulfoxide	solvent	Hammett σ -value	reference
 26	$X-C_6H_4-SOMe$	benzene	+ 0.52	present study
Me_3COO^-	$(X-C_6H_4)_2SO$	toluene	+ 1.4 ^a	b
	$X-C_6H_4-SOPh$	dioxane-water	+ 0.71	c
 (fluorenone oxide)	$(X-C_6H_4)_2SO$	benzene	+ 0.26	d
	$(X-C_6H_4)_2SO$	benzene	+ 0.25	e
	$(X-C_6H_4)_2SO$	benzene	+ 0.23	e

^aFor the reaction of di-substituted diphenyl sulfoxides with Me_3COO^- , σ was calculated from the relative rates at 40°C given in this paper plotting $\log k_{rel}$ vs. σ . σ -values given in references d and e were calculated also in this way. ^bR. Curi, F. DiFuria, and G. Modena, J. Chem. Soc., Perkin II, 603 (1978). ^cR. Curi and G. Modena, Gazz. Chim. Ital., 94, 1257 (1964). ^dY. Sawaki, H. Kato, and Y. Ogata, J. Am. Chem. Soc., 103, 3832 (1981). ^eY. Sawaki and Y. Ogata, Ibid, 103, 5947 (1981).

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